

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-071416
(43)Date of publication of application : 21.03.2001

(51)Int.Cl. B32B 15/20
B32B 15/08
C08G 61/08

(21)Application number : 11-249437 (71)Applicant : HITACHI CHEM CO LTD
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(54) PRODUCTION OF COPPER-CLAD LAMINATED BOARD

(57)Abstract:
PROBLEM TO BE SOLVED: To easily produce a copper-clad laminate board having an insulating layer of cycloolefins by using a molding material produced by using a specified metathesis polymerization catalyst.
SOLUTION: A copper-clad laminated board having an insulating layer of cycloolefins is formed by a process in which a semi-cured curable molding material is manufactured by reacting metathesis-polymerizable cycloolefins in the presence of a metathesis polymerization catalyst, after copper foil is arranged at least on one side of the molding material, heated and pressed. Norbornens having at least two rings or at least one selected from $\geq 4C$ monocyclic cycloolefins are used as the cycloolefins. A polymerizable composition containing cycloolefins and the catalyst can produce a copper-clad laminated board by a usual press molding machine and can be molded without attaching a special apparatus for shutting out oxygen and water in air which hinder the polymerization to the molding machine.

LEGAL STATUS

[Date of request for examination]
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
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CLAIMS

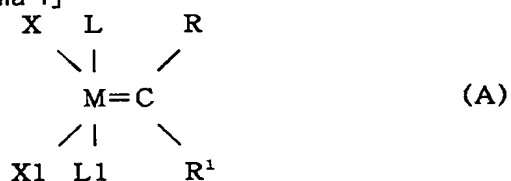
[Claim(s)]

[Claim 1] The manufacture approach of a copper-clad laminate of performing heating and pressurization after arranging copper foil at least to one side of the shaping material which the cycloolefins in which a metathesis polymerization is possible were made reacting, and was made into the semi-hardening condition under existence of a metathesis polymerization catalyst and which can be hardened.

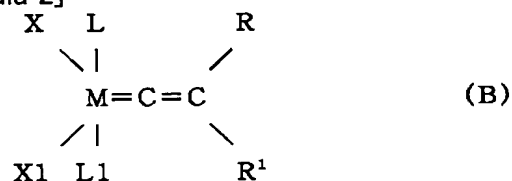
[Claim 2] The manufacture approach of a copper-clad laminate according to claim 1 that the cycloolefins in which a metathesis polymerization is possible contain a dicyclopentadiene.

[Claim 3] The manufacture approach of a copper-clad laminate according to claim 1 or 2 of the metathesis polymerization catalyst as which a metathesis polymerization catalyst is expressed in a general formula (A) or a general formula (B) of being a kind at least.

[Formula 1]



[Formula 2]



(In a general formula (A) and (B) ruthenium or osmium; R and R1 M) Independently, respectively Hydrogen, the alkyl group of carbon numbers 1-20, the alkenyl radical of carbon numbers 2-20,

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CLAIMS

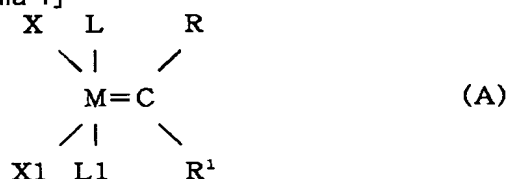
[Claim(s)]

[Claim 1] The manufacture approach of a copper-clad laminate of performing heating and pressurization after arranging copper foil at least to one side of the shaping material which the cycloolefins in which a metathesis polymerization is possible were made reacting, and was made into the semi-hardening condition under existence of a metathesis polymerization catalyst and which can be hardened.

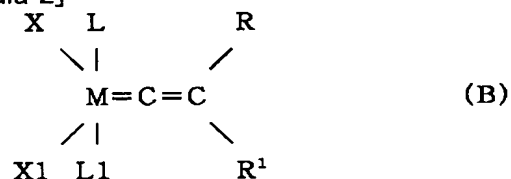
[Claim 2] The manufacture approach of a copper-clad laminate according to claim 1 that the cycloolefins in which a metathesis polymerization is possible contain a dicyclopentadiene.

[Claim 3] The manufacture approach of a copper-clad laminate according to claim 1 or 2 of the metathesis polymerization catalyst as which a metathesis polymerization catalyst is expressed in a general formula (A) or a general formula (B) of being a kind at least.

[Formula 1]



[Formula 2]



(In a general formula (A) and (B) ruthenium or osmium; R and R¹ M) Independently, respectively Hydrogen, the alkyl group of carbon numbers 1-20, the alkenyl radical of carbon numbers 2-20, The alkynyl group of carbon numbers 2-20, an aryl group, the carboxylate radical of carbon numbers 1-20, The alkoxy group of carbon numbers 1-20, the alkenyloxy radical of carbon numbers 2-20, An aryloxy group, the alkoxy carbonyl group of carbon numbers 2-20, the alkylthio group of carbon numbers 1-20, The alkyl sulfonyl radical of carbon numbers 1-20, the alkyl sulfinyl group of carbon numbers 1-20, It is chosen out of the alkyl seleno radical of carbon numbers 1-20, the alkyl SERENINIRU radical of carbon numbers 1-20, or the alkyl seleno nil radical of carbon numbers 1-20. Each may be permuted by the alkoxy group or phenyls of the alkyl group of carbon numbers 1-5, a halogen, and carbon numbers 1-5. ;X by which said phenyls may be permuted by the halogen, the alkyl group of carbon numbers 1-5, and the alkoxy group of carbon numbers 1-5, and X¹ show the electron donative group of neutrality [1 / anionic ligand; L and / L].

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of manufacturing a copper-clad laminate from the cycloolefins in which a metathesis polymerization is possible.

[0002]

[Description of the Prior Art] Conventionally, after sinking phenol resin, an epoxy resin, polyimide resin, etc. into base materials, such as glass and paper, with the press-forming machine, heating and pressurization were performed to coincidence and the copper-clad laminate was manufacturing them.

[0003] On the other hand, the metathesis polymerization of the norbornene mold cycloolefins (monomer), such as a dicyclopentadiene, is carried out, and the method of obtaining a copper-clad laminate is also learned. for example, the solution B which changes from the solution A which consists of the catalyst component of a metathesis catalyst system, and mixture with a monomer, the activator of a metathesis catalyst system, and mixture with a monomer to JP,62-52987,A -- reaction injection molding (RIM) -- the method of manufacturing a printed wired board by law is indicated. As a catalyst component of the metathesis catalyst system used at this time, there are a tungsten, organic ammonium salt of molybdenum, etc., and organoaluminium compounds, such as alkoxy alkylaluminum halide and aryloxy aluminum halide, are indicated as an activation component. Thus, the copper-clad laminate which is made to carry out the bulk polymerization of the norbornene mold cycloolefins (monomer), such as an obtained dicyclopentadiene, and is obtained is excellent in an electrical property, solder thermal resistance, etc.

[0004] By the above mentioned metathesis catalyst system, it turns out that a catalyst component is activated with an activator and ring opening polymerization of the norbornene mold monomer is carried out. Moreover, when performing the above-mentioned reaction injection molding, collision mixing of Solution A and the solution B is carried out, immediately, the mixed liquor is poured in, while it has been liquefied in metal mold, it is massive and ring opening polymerization is carried out.

[0005]

[Problem(s) to be Solved by the Invention] However, if the organoaluminium compound used as the above-mentioned activator has high reactivity and water and oxygen exist, it will react with these immediately and a catalytic activity-ized operation will be lost. Then, in order to make it lose catalytic activity neither by water nor oxygen, when performing reaction injection molding, the water in atmospheric air and mixing of oxygen must be eliminated as much as possible. Therefore, it is necessary using assembled-die metal mold to carry out a bulk polymerization all over the space formed where the metal mold is closed. Moreover, since it manufactured the one manufacture approach of the above mentioned copper-clad laminate at a time by reaction injection molding, the press-forming machine usually used could not be used for it, and it was not able to manufacture many copper-clad laminates at once. Press forming used for the conventional copper-clad laminate usual is used for this invention, without using equipments, such as reaction injection molding, and it offers the approach of manufacturing easily the copper-clad laminate which made cycloolefins the insulating layer.

[0006]

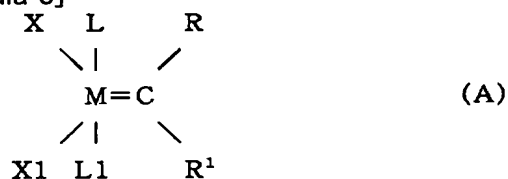
[Means for Solving the Problem] As a result of examining many things that the above-mentioned technical problem should be solved, this invention persons manufacture the shaping material of a semi-hardening condition which has a specific degree of hardness using a specific metathesis polymerization catalyst like Ru (ruthenium) carbene catalyst, and came to complete a header and this invention for the manufacture approach of the copper-clad laminate using this shaping material.

[0007] That is, this invention relates to the manufacture approach of a copper-clad laminate of performing heating and pressurization, after arranging copper foil at least to one side of the shaping material which the cycloolefins in which a metathesis polymerization is possible were made to react, and was made into the semi-

hardening condition under existence of a metathesis polymerization catalyst which can be hardened. And when the cycloolefins in which a metathesis polymerization is possible contain a dicyclopentadiene, it is the manufacture approach of the desirable above-mentioned copper-clad laminate. Moreover, a metathesis polymerization catalyst is the manufacture approach of the as desirable above-mentioned copper-clad laminate which is the metathesis polymerization catalyst expressed with a general formula (A) or a general formula (B) as being a kind at least.

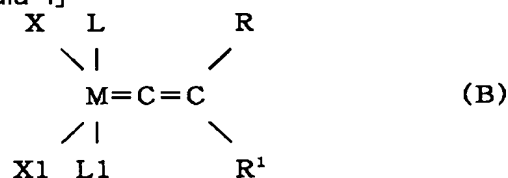
[0008]

[Formula 3]



[0009]

[Formula 4]



(In a general formula (A) and (B) ruthenium or osmium; R and R¹ M) Independently, respectively Hydrogen, the alkyl group of carbon numbers 1-20, the alkenyl radical of carbon numbers 2-20, The alkynyl group of carbon numbers 2-20, an aryl group, the carboxylate radical of carbon numbers 1-20, The alkoxy group of carbon numbers 1-20, the alkenyloxy radical of carbon numbers 2-20, An aryloxy group, the alkoxy carbonyl group of carbon numbers 2-20, the alkylthio group of carbon numbers 1-20, The alkyl sulfonyl radical of carbon numbers 1-20, the alkyl sulfinyl group of carbon numbers 1-20, It is chosen out of the alkyl seleno radical of carbon numbers 1-20, the alkyl SERENINIRU radical of carbon numbers 1-20, or the alkyl seleno nil radical of carbon numbers 1-20. Each may be permuted by the alkoxy group or phenyls of the alkyl group of carbon numbers 1-5, a halogen, and carbon numbers 1-5. ;X by which said phenyls may be permuted by the halogen, the alkyl group of carbon numbers 1-5, and the alkoxy group of carbon numbers 1-5, and X1 show the electron donative group of neutrality [1 / anionic ligand; L and / L].

[0010]

[Embodiment of the Invention] As cycloolefins which are used by this invention and in which a metathesis polymerization is possible, as being chosen out of the norbornene of two or more ring formations, or with a carbon numbers of four or more monocycle cycloolefins, a kind can be used as it is few. Norbornene, such as a permutation or unsubstituted norbornene, a dicyclopentadiene, and a dihydrodicyclopentadiene, is used suitably. Since the reinforcement of a laminate improves in order to form a three-dimensions bridge formation moldings after carrying out a metathesis polymerization, a dicyclopentadiene is used especially suitably. As amount of the dicyclopentadiene used, it is more than 10 weight sections among the cycloolefins in which a metathesis polymerization is possible, and they are more than 50 weight sections especially preferably more than 30 weight sections preferably.

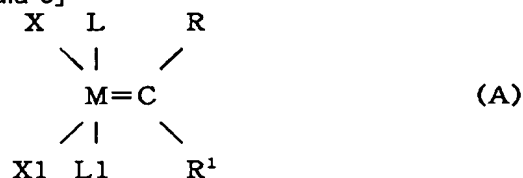
[0011] As norbornene, norbornene, norbornadiene, methyl norbornene, Dimethyl norbornene, ethyl norbornene, ethylidene norbornene, Butyl norbornene, 5-acetyl-2-norbornene, dimethyl-5-norbornene -2, a 3-dicarboxy rate, N-hydroxy-5-norbornene -2, 3-dicarboxyimide, 5-norbornene-2-carbonitrile, a 5-norbornene-2-carboxy aldehyde, 5-norbornene -2, 3-dicarboxylic acid monomethyl ester, 5-norbornene -2, 3-dicarboxylic acid dimethyl ester, 5-norbornene -2, 3-dicarboxylic acid diethyl ester, 5-norbornene -2, 3-dicarboxylic acid di-n-butyl ester, 5-norbornene -2, 3-dicarboxylic acid dicyclohexyl ester, 5-norbornene -2, 3-dicarboxylic acid dibenzyl ester, 5-norbornene -2, 3-dicarboxylic acid anhydride, 3, 6-epoxy - 1, 2, 3, 6-tetrahydrophthalic anhydride, 5-norbornene -2, 3-dicarboxylic acid, a 5-norbornene-2-methanol, 2 ring norbornene, such as 6-triethoxy silyl-2-norbornene and 5-norbornene-2-oar, A dicyclopentadiene (dimer of a cyclopentadiene), a dihydrodicyclopentadiene, 3 ring norbornene, such as a methyl dicyclopentadiene and a dimethyl dicyclopentadiene, 4 ring norbornene, such as tetracyclo dodecen, methyl tetracyclo dodecen, and dimethyl cyclo tetra-dodecen, The norbornene of five or more rings, such as tricyclo pentadiene (trimer of a cyclopentadiene) and tetracyclo pentadiene (tetramer of a cyclopentadiene), is mentioned.

[0012] The compound which has two or more norbornene radicals, for example, tricyclo dodeca diene, symmetry mold tricyclo pentadiene, etc. can also be used. Cyclobutenes other than norbornene, cyclopentene, cyclooctane, Cyclo dodecen, 1, 5-cyclo-octadiene, 1, 3 and 5, 7-cyclo-octatriene, 1, 5, 7-cyclododecatriene, 5, 6-epoxy-1-cyclooctane, 3, 4-epoxy-1-cyclooctane, 5-methoxy-1-cyclooctane, 5-BUROMO-1-cyclooctane, 5-isopropoxy-1-cyclooctane, 5-formyl-1-cyclooctane, 5-methoxy-1-cyclooctane, Cycloolefins, such as (trimethylsilyl)-cyclo oct-1-en-5-carboxylate, a tetrahydro indene, and a methyl tetrahydro indene, can be used. The above compound can also be independently used as two or more mixture again.

[0013] Even if there are few metathesis polymerization catalysts the metathesis polymerization catalysts used by this invention are indicated to be by the general formula (A) and the general formula (B), a kind is used preferably.

[0014]

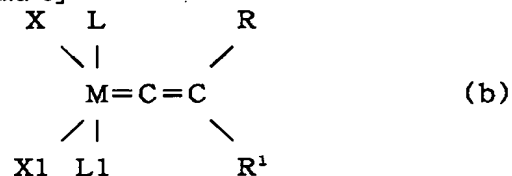
[Formula 5]



(Here, ruthenium or osmium; R and R1 M) Independently, respectively Hydrogen, the alkyl group of carbon numbers 1-20, the alkenyl radical of carbon numbers 2-20, The alkynyl group of carbon numbers 2-20, an aryl group, the carboxylate radical of carbon numbers 1-20, The alkoxy group of carbon numbers 1-20, the alkenyloxy radical of carbon numbers 2-20, An aryloxy group, the alkoxy carbonyl group of carbon numbers 2-20, the alkylthio group of carbon numbers 1-20, It is chosen out of the alkyl sulfonyl radical of carbon numbers 1-20, or the alkyl sulfinyl group of carbon numbers 1-20. Each may be permuted by the alkoxy group or phenyls of the alkyl group of carbon numbers 1-5, a halogen, and carbon numbers 1-5. ;X by which said phenyls may be permuted by the halogen, the alkyl group of carbon numbers 1-5, and the alkoxy group of carbon numbers 1-5, and X1 show the electron donative group of neutrality [1 / anionic ligand; L and / L].

[0015]

[Formula 6]



(Here, ruthenium or osmium; R and R1 M) Independently, respectively Hydrogen, the alkyl group of carbon numbers 1-20, the alkenyl radical of carbon numbers 2-20, The alkynyl group of carbon numbers 2-20, an aryl group, the carboxylate radical of carbon numbers 1-20, The alkoxy group of carbon numbers 1-20, the alkenyloxy radical of carbon numbers 2-20, An aryloxy group, the alkoxy carbonyl group of carbon numbers 2-20, the alkylthio group of carbon numbers 1-20, The alkyl sulfonyl radical of carbon numbers 1-20, the alkyl sulfinyl group of carbon numbers 1-20, It is chosen out of the alkyl seleno radical of carbon numbers 1-20, the alkyl SERENINIRU radical of carbon numbers 1-20, or the alkyl seleno nil radical of carbon numbers 1-20. Each may be permuted by the alkoxy group or phenyls of the alkyl group of carbon numbers 1-5, a halogen, and carbon numbers 1-5. ;X by which said phenyls may be permuted by the halogen, the alkyl group of carbon numbers 1-5, and the alkoxy group of carbon numbers 1-5, and X1 show the electron donative group of neutrality [1 / anionic ligand; L and / L].

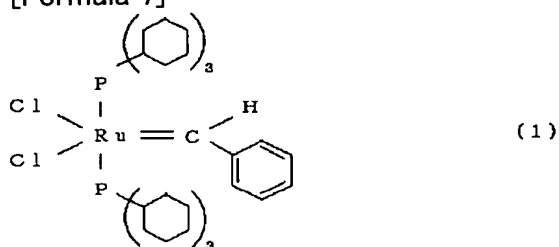
[0016] The anionic ligand in X and X1 is a radical with an electronegative charge, when the coordination to a central metal is removed. As such a radical, for example Hydrogen, a halogen, CF3CO2, CH3CO2, CFH2CO2, 3 (CH3) CO, 2(CH3) CO, 2(CH3 (CF3)) CO, the alkyl group of carbon numbers 1-5, (CF3) There are the alkoxy group of carbon numbers 1-5, a phenyl group, a phenoxy group, a tosyl group, a mesyl radical, a trifluoromethane sulfonate radical, etc., and both of especially a desirable thing are halogens (especially chlorine). Moreover, the neutral electron donative group in L and L1 in a general formula (A) and a general formula (B) is a radical with a neutral charge, when the coordination to a central metal is removed. as such a radical -- PR two R3R4 (here -- it is -- R2 -- the alkyl group of the 2nd class, or a cycloalkyl radical --) R3 and R4 show an aryl group, the 1st class alkyl group of carbon numbers 1-10 or the 2nd class alkyl group, and a cycloalkyl radical independently, respectively. There are a phosphine system electron donative group expressed, a pyridine, p-fluoro pyridine, etc.,

and, for both, especially a desirable thing is. – It is P(cyclohexyl)₃, –P(cyclopentyl)₃, or –P(isopropyl)₃. As for the above-mentioned metal mold carbene catalyst, what used the ruthenium for the metal from economical efficiency or the point of the ease of carrying out of acquisition rather than molybdenum is desirable.

[0017] Unlike the double decomposition catalyst system of 2 liquid system which combined a catalyst component which is known conventionally, and the activator, these metathesis polymerization catalyst can carry out ring opening polymerization of the metathesis polymerization nature compound at a double decomposition (metathesis) reaction, without losing catalytic activity easily with oxygen and the moisture in air. The concrete thing of a metathesis polymerization catalyst has the desirable thing which is the catalyst which is mentioned to for example, formula (1) – (8) and to mention to especially a formula (3).

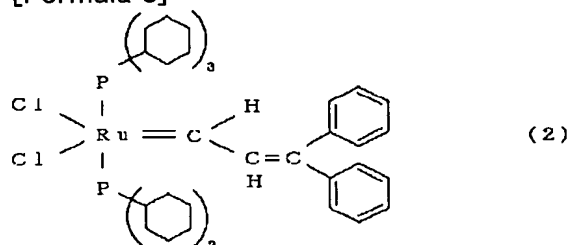
[0018]

[Formula 7]



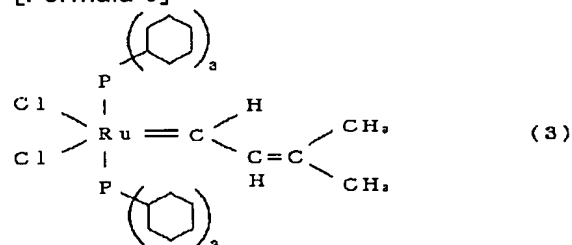
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[Formula 8]



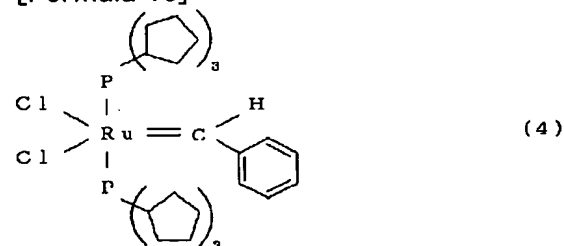
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[Formula 9]



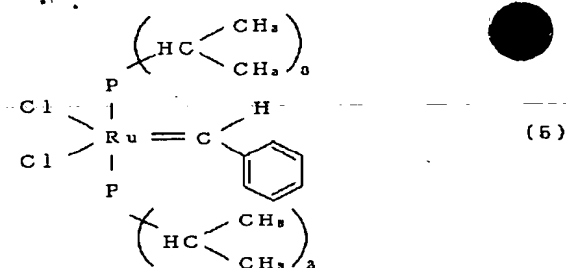
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[Formula 10]



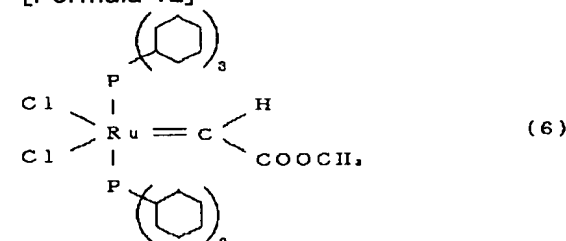
[0022]

[Formula 11]



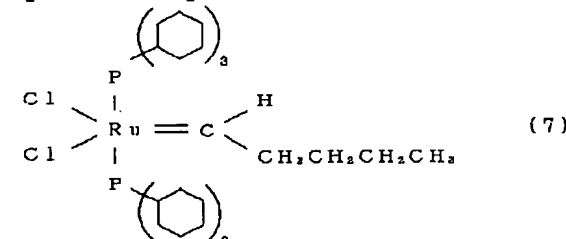
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[Formula 12]



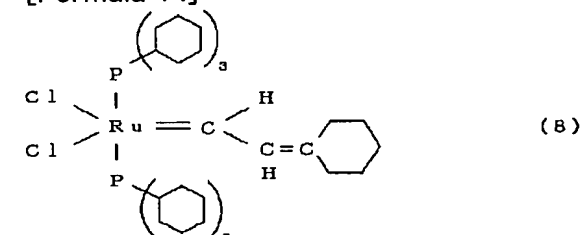
[0024]

[Formula 13]



[0025]

[Formula 14]



[0026] A metathesis polymerization catalyst can be independently used combining two or more kinds. this time -- the cycloolefins 100 weight section in which the metathesis polymerization of the amount of catalysts is possible -- receiving -- 0.001 - 20 weight section -- it is 0.01 - 5 weight section preferably. In under the 0.001 weight section, if hardening becomes poor and 20 weight sections are exceeded, it is uneconomical. The above-mentioned metal carbene compound can be obtained with a well-known synthesis method. For example, ORGANO METARIKKUSU (Organometallics) The approach of using the 16th volume, No. 18, and the propargyl chloride shown in 3867 pages (1997) is mentioned.

[0027] The synthetic example of a catalyst is shown below. (Synthetic example) 500ml Fisher-Porter sec-butanol 250ml which removed cyclo-octadiene ruthenium dichloride (21mmol), tri-cyclohexyl phosphine (42mmol), a sodium hydroxide (7.2g), and oxygen is put into bottle, and it heats at 90 degrees C under a hydrogen 2 atmospheric pressure. Pressurization is repeated several times until absorption of hydrogen is completed, and churning is continued overnight. It cools to a room temperature, with the pressure of hydrogen put, and the precipitate of light yellow is obtained. 30ml of water is added, precipitate is filtered, it dries in a hydrogen air current, and Ru(H)2(H2)2(Pcy)2 are obtained (Pcy3 shows three cyclohexyl radicals (cy) combined with the Lynn atom P about 80% of yield, and here). Next, this Ru(H)2(H2)2(Pcy)2 (1.5mmol) is dissolved in 30ml of dichloroethane solutions, and it cools at -30 degrees C. A 3-chloro-3-methyl-1-butyne (1.5mmol) is added. A solution changes to purplish red immediately and is made to react for 15 minutes as it is. If the methanol (20ml) which removed and carried out degasifying of the cooling bath is added, a purple crystal will

precipitate. It is made to wash and with a methanol and Ru carbene catalyst $(\text{CH}_3)_2\text{Ru}=\text{CH}-\text{CH}=\text{C}(\text{CH}_3)_2$ of said general formula (C) is obtained (95% of yield). (Bibliography: The 4th volume (Organometallics) of ORGANO METARIKKUSU, No. 18, 3867 pages (1997))

[0028] In the manufacture approach of the copper-clad laminate of this invention, although the above-mentioned cycloolefins in which a metathesis polymerization is possible and an above-mentioned metathesis polymerization catalyst are an indispensable component, reinforcement, such as a filler, a glass fiber, a glass fabric, a paper base, and a nonwoven glass fabric, can be used if needed. Moreover, a coupling agent, an antioxidant, a flame retarder, a release agent, a coloring agent, light stabilizer, etc. can be added in the range which does not spoil the purpose of this invention. In addition, additives, such as reforming material and a reaction regulator, can be added if needed.

[0029] As reforming material, a rubber system elastomer, polystyrene, saturated polyester, polyethylene, polyimide, acrylic resin, methacrylic resin, vinyl resin, an epoxy resin, polyamide resin, triazine resin, etc. can be used. As a reaction regulator, triphenylphosphine, tricyclohexyl phosphoretted hydrogen, tricyclo pentyl phosphoretted hydrogen, tributyl phosphoretted hydrogen, triisopropyl phosphoretted hydrogen, etc. can be used, and 0.001 – 10 weight section can usually be added to the cycloolefins 100 weight section. The copper foil used by this invention can use the copper foil usually used for a copper-clad laminate, and especially a limit will be in thickness and a roughening condition. Moreover, the front face may be processed with a silane coupling agent, a titanate system coupling agent, and various adhesives.

[0030] Although it has the shape of a solid without a fluidity (it does not deform with a self-weight) at a room temperature, the shaping material which can be hardened in the state of the semi-hardening of this invention is shaping material which can do secondary size enlargement easily, a metathesis reaction can progress with heating, and can manufacture a hardened material (mold goods) with the configuration of secondary size enlargement, and can manufacture a copper-clad laminate by performing press forming with copper foil at this time. If a metathesis polymerization catalyst which was described above is used, the rate of a metathesis polymerization reaction can be adjusted to arbitration by choosing suitably conditions (use of the amount of the catalyst used, reaction temperature, and a reaction adjustment (control) agent etc.). Therefore, the condition (semi-hardening condition) in the middle of the polymerization (metathesis) reaction of raw material cycloolefins not being completed can be built. The process which builds this semi-hardening condition is the first process. Easily, the shaping material of a semi-hardening condition can do secondary size enlargement, if it heats, a metathesis polymerization reaction can resume, and can complete hardening, and can be used as mold goods. The process which arranges copper foil at least to one side at this process that secondary size enlargement is carried out [process] and completes hardening, and manufactures a copper-clad laminate by heating pressurization is the second process. Although the shaping material of a semi-hardening condition has the shape of a solid without a fluidity at a room temperature, it has easily the hardness (degree of hardness) in which secondary size enlargement is possible. The hardness of the shaping material of this invention can be suitably chosen according to the approach of secondary size enlargement, or the configuration of mold goods. If the degree of hardness of the shaping material which was made into the semi-hardening condition of the shaping material of this invention and which can be hardened is 75 or less and becomes hard more than this with the measured value of a rubber hardness meter (GS-702N, JIS K7215 D type), secondary size enlargement will become difficult. 50 or less are desirable at the measured value of a rubber hardness meter (GS-702N, JIS K7215 D type). Furthermore, it becomes difficult it to maintain the configuration of secondary size enlargement, if the degree of hardness of this shaping material is 50 or more and becomes soft from this with the measured value of an elasticity hardness meter (GS-701G, JIS S6050). 60 or more are desirable at the measured value of an elasticity hardness meter (GS-701G, JIS S6050). Hardness of the shaping material of a semi-hardening condition can be designed and adjusted in the range of desired by choosing suitably the conditions (use of the amount of the catalyst used, a reaction and a storage temperature, and a reaction adjustment (control) agent etc.) of the first process.

[0031] At the first process, the liquefied compound which mixed the additive raw material cycloolefins, a metathesis polymerization catalyst, and if needed is heated. The temperature of heating is continued until the range of congealing-point -60 degree C of a compound will be in the semi-hardening condition whose fluidity of a compound is usually lost preferably. If the temperature of the first process is raised too much, crosslinking reaction will advance with a linear polymer formation reaction, and it remains [the degree of hardness of shaping material becomes high too much, or / many unreacted objects] into the last hardened material and is not desirable. The range of the setting time is several hours from several minutes, and it can be suitably adjusted according to an activity gestalt, a production facility, etc. The first process includes the process kept under a predetermined temperature ambient atmosphere until shaping material becomes a predetermined degree of hardness, after heating of a compound is completed. The temperature of storage is -30 degrees C – 60 degrees

C, and is 0 degree C – 50 degrees C preferably. The time amount of storage can be suitably chosen according to the gestalt of production in the range from 3 minutes by five months, and is 20 minutes – 30 days preferably.

[0032] At the second process, copper foil is arranged at least to one side of the shaping material which the first process completed, heating pressurization is carried out, and a hardening reaction is completed. The range of the heating temperature for fully advancing a hardening reaction is 100 degrees C – 250 degrees C, and it is 130 degrees C – 200 degrees C preferably. Although the setting time of the second process is based also on a reaction rate, in order to fully advance hardening, it is desirable to carry out for 10 minutes to 2 hours.

Moreover, although there is especially no convention as a pressure when pressurizing, it is desirable to carry out in the range of 10 kg/cm² – 100 kg/cm².

[0033]

[Example] An example explains this invention below. In addition, among an example, especially the section means the weight section, unless it limits. In addition, the hardened material obtained in each example and the example of a comparison evaluated the test piece by the following approaches. (A) Before performing the second process of degree-of-hardness evaluation, the degree of hardness of a test piece (the number of measurement places is ten points) was measured.

(1) Rubber hardness meter (GS-702N, JIS K7215 D type)

(2) Elasticity hardness meter (GS-701G, JIS S6050)

[0034] (Example)

(Dicyclopentadiene resin liquid) The triphenyl phosphine 0.125 weight section was added in the dicyclopentadiene (referred to as DCPD) 100 weight section of about 99 % of the weight of commercial purity, and DCPD Resin liquid was produced.

(Production of a test piece) 0.085 weight section addition of the Ru carbene catalyst shown by the formula (1) described above in the above-mentioned DCPD Resin liquid 100 weight section was carried out, it stirred for 2 minutes, and the catalyst was dissolved completely. This DCPD Resin liquid was poured into two glass plates (300mmx300mmx6mm) and the casting glass plate which formed space with the spacer with a thickness of 1mm. It was made to react in 40 degrees C and a 30-minute dryer, and the shaping material of a semi-hardening condition was obtained (the first process). As a result of measuring the degree of hardness at this time with a rubber hardness meter and an elasticity hardness meter, it was 44 and 99, respectively. After ending the first process, press forming was carried out by 50 kg/cm² by the copper foil of copper foil (18 micrometers in thickness) for 150 degrees C and 1 hour, and the copper-clad laminate was manufactured. The property of the copper-clad laminate at that time was shown in Table 1. A property is JIS. It measured according to C6481, copper foil was etched, and after making it the electrode or etching and removing copper foil in the bending test, it measured.

[0035]

[Table 1]

項目	測定値
銅箔引き剥かし強さ (Kg/cm)	1. 1
誘電率 (1MHz)	2. 5
誘電正接 (1MHz)	0. 0007
体積抵抗率 (Ω・cm)	5×10 ¹⁵
絶縁破壊の強さ (KV/mm)	40
曲げ強さ (MPa)	108
曲げ弾性率 (GPa)	2. 4

[0036]

[Effect of the Invention] The polymerization nature constituent which includes a cycloolefin and a metathesis polymerization catalyst according to the manufacture approach of the copper-clad laminate of this invention could produce the copper-clad laminate with the usual press-forming machine, and it could fabricate it, without attaching the special equipment for moreover intercepting oxygen and the moisture in the air which checks a polymerization reaction to a press-forming machine, and circuit formation by the etching method usually used was possible for the manufactured copper-clad laminate.

[Translation done.]

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